DESCRIPTION

Ni-BASE SUPERALLOY AND GAS TURBINE COMPONENT USING THE SAME

TECHNICAL FIELD

[0001]

The present invention relates to a Ni-base superalloy having an excellent resistance to corrosion at high temperatures, an excellent resistance to oxidation at high temperatures, and high-temperature strength, and gas turbine component using the same, in order to deal with low-quality fuel.

BACKGROUND ART

[0002]

The Ni-base superalloy is widely used as industrial gas turbine components, for example, turbine blade materials such as Rene80 and IN792 having an excellent resistance to corrosion, Mar-M247 having an excellent resistance to oxidation and a high strength are known.

Further, CMSX-11 having both a good resistance to corrosion and a high strength realized by single crystal casting of the high chromium content alloy is also known.

[0003]

These existing Ni-base superalloys cannot share the properties of the high resistance to corrosion (Rene80, etc.) and the high resistance to oxidation and high strength (Mar-M247, etc.), so that there is a failure that they cannot be applied to improve the efficiency of a gas turbine dealing with low-quality fuel such as heavy oil.

Further, an alloy (CMSX-11, etc.) having a resistance to corrosion and a strength realized by single crystal casting of the high chromium content alloy does not have a sufficient resistance to oxidation, and moreover there is a problem with single-crystal material that the casting yield of components in complicated shapes is lowered.

[0004]

To solve the problems of the existing Ni-base superalloys, a high corrosion resistant and high strength alloy containing, by weight % (wt%), Cr: 6 to 12%, Al(aluminum): 4.5 to 6.5%, W(tungsten): 2 to 12%, Ta(tantalum): 2.5 to 10%, Mo(molybdenum): up to 5.8%, Co(cobalt): 0.1 to 3%, Nb(niobium): 0.2 to 3%, Re(rhenium): 0.1 to 4%, and Hf(hafnium): up to 0.3%, having a P value (calculated by weight % by Formula (1) indicated below) of 2350 to 3280, and the balance of Ni and inevitable impurities is known.

$$P = 200Cr + 80Mo - 20Mo^2 - 250Ti^2 - 50(Ti \times Ta) + 15Nb + 200W - 14W^2 + 30Ta - 1.5Ta^2 + 2.5Co + 1200Al - 100Al^2 + 100Re + 1000Hf - 2000Hf^2 + 700Hf^3 - 2000V - 500C - 15000B - 500Zr \quad \text{---} \quad (1)$$

However, this high corrosion resistant and high strength alloy does not contain Titanium, so that the resistance to corrosion in a high-temperature corrosive environment where oxidation and sulfidation are superimposed is insufficient.

[0005]

Further, a large casting of columnar grained Ni-base heat resistant alloy having an excellent high-temperature resistance to intergranular corrosion, containing, by weight %, Cr: 12.0 to 14.3%, Co: 8.5 to 11.0 %, Mo: 1. 0 to 3.5%, W: 3.5 to 6.2%, Ta: 3.0 to 5.5%, Al: 3.5 to 4.5%, Ti: 2.0 to 3.2%, C(carbon): 0.04 to 0.12%, B(boron): 0.005 to 0.05%, and Zr(zirconium): 0.001 to 5 ppm and the balance of Ni and inevitable impurities is known.

However, in the large casting of columnar grained Ni-based heat resistant alloy, the quantity ratio of Cr, Al, and Ti is inappropriate, so that the resistance to corrosion and the resistance to oxidation cannot coexist with each other.

[0006]

Furthermore, a Ni series supper-alloy suitable for single-crystal solidification containing, by weight %, Co: 4.75 to 5.25%, Cr: 15.5 to 16.5%, Mo: 0.8 to 1.2%, W: 3.75 to 4.25%, Al: 3.75 to 4.25%, Ti: 1.75 to 2.25%, Ta: 4.75 to 5.25%, C: 0.006 to 0.04%, B: up to 0.01%, Zr: up to 0.01%,

Hf: up to 1%, Nb: up to 1%, and Ni and impurity components added so as to reach 100% in total is known.

However, this Ni series super-alloy contains Cr too much, so that the resistance to oxidation is insufficient.

[0007]

Furthermore, a high corrosion resistance Ni-based single crystal supper-alloy containing, by weight %, Cr: 8 to 14%, Co: 3 to 7%, Al: 4 to 8%, Ti: up to 5%, W: 6 to 10%, Ta: 4 to 8%, Mo: 0.5 to 4%, Hf: up to 1.4%, Zr: up to 0.01%, C: up to 0.07%, B: up to 0.015%, and the balance of Ni and inevitable impurities, wherein 5% ≤ Al + Ti, 4 ≤ Al/Ti, and W + Ta + Mo ≤ 18% is known. However, the Ni-based single crystal super-alloy is deficient in Ti due to the restriction of 4 ≤ Al/Ti, so that the resistance to corrosion is insufficient.

[0008]

Further, a Ni-based super-alloy containing, by weight %, Cr: 7 to 12%, Co: 5 to 15%, Mo: 0.5 to 5%, W: 3 to 12%, Ta: 2 to 6%, Ti: 2 to 5%, Al: 3 to 5%, Nb: up to 2%, Hf: up to 2%, C: 0.03 to 0.25%, and B: 0.002 to 0.05% and composed of residual components of Ni and accompanying impurities is known.

Although it is said that this Ni-based super-alloy is improved in the balance between the resistance to oxidation and the resistance to corrosion by an increase in the ratio of Al to Ti, the relation to the element added to increase the strength is not taken into account.

[0009]

Furthermore, a Ni-based alloy containing, by weight %, Cr: 2 to 25%, Al: 1 to 7%, W: 2 to 15%, Ti: 0.5 to 5%, Nb: up to 3%, Mo: up to 6%, Ta: 1 to 12%, Re: up to 4%, Co: 7.5 to 25%, Fe(iron): up to 0.5%, C: up to 0.2%, B: 0.002 to 0.035%, Hf: up to 2.0%, Zr: 0.02%, and Ni: 40% or more is known.

However, in this Ni-based alloy, the relationship between the balance of elements and the material properties is not taken into account.

[0010]

As documents concerning the background art, Japanese

Patent Publication No. 2843476, Japanese Patent Publication No. 3246376, Japanese Patent Laid-Open Publication No. 2002-235135, Japanese Patent Laid-Open Publication No. 7-300639, Japanese Patent Laid-Open Publication No. 5-59473, and Japanese Patent Laid-Open Publication No. 9-170402 may be cited.

DISCLOSURE OF THE INVENTION

[0011]

The present invention is intended to provide, as a component material of an industrial gas turbine, a Ni-base superalloy having an excellent resistance to hot corrosion with low-quality fuel and an excellent resistance to oxidation at high temperatures and a high-temperature strength to improve the thermal efficiency, also having a high yield at the precision casting process, and gas turbine component using the same.

[0012]

To solve the problem aforementioned, the first Ni-base superalloy of the present invention consists essentially of: by weight %, Co: 9 to 11%, Cr: 9 to 12%, Mo: up to 1%, W: 6 to 9%, Al: 4 to 5%, Ti: 4 to 5%, Nb: up to 1%, Ta: up to 3%, Hf: 0.5 to 2.5%, Re: up to 3%, C: 0.05 to 0.15%, B: 0.005 to 0.015%, Zr: up to 0.05%, and the balance of Ni and inevitable impurities.

Further, the weight % of Hf is preferably 0.5 to 1%.

[0013]

To solve the problem aforementioned, the second Ni-base superalloy of the present invention consists essentially of: by weight %, Co: 9 to 10%, Cr: 9 to 10%, Mo: 0.5 to 1%, W: 6 to 8%, Al: 4 to 5%, Ti: 4 to 5%, Ta: 2 to 3%, Hf: 0.5 to 2.5%, Re: 1 to 3%, C: 0.05 to 0.1%, B: 0.005 to 0.01%, Zr: up to 0.02%, and the balance of Ni and inevitable impurities.

Further, the weight % of Hf is preferably 0.5 to 1%.

[0014]

To solve the problem aforementioned, the third Ni-base

superalloy of the present invention consists essentially of: by weight %, Co: 10 to 11%, Cr: 10 to 12%, W: 8 to 9%, Al: 4 to 5%, Ti: 4 to 5%, Nb: up to 1%, Hf: 0.5 to 2.5%, C: 0.05 to 0.15%, B: 0.005 to 0.015%, Zr: 0.01 to 0.05%, and the balance of Ni and inevitable impurities.

Further, the weight % of Hf is preferably 0.5 to 1%.

[0015]

To solve the problems aforementioned, the gas turbine component of the present invention is manufactured by using any of the first to third Ni-base superalloys aforementioned and is preferably manufactured by using the directional solidification casting method.

[0016]

The present invention was developed, to realize the coexistence of the resistance to corrosion at high temperatures and the resistance to oxidation at high temperatures and high-temperature strength, by producing and evaluating many alloys by way of trial, as a result, adjusting the quantity ratio of Cr, Al, and Ti to an appropriate range, within the composition range, finding that W is effective as an element for contributing to strength improvement and little badly affecting the resistance to corrosion, and furthermore taking the phase stability judged from the solid solution quantity to the γ (gamma) phase and γ' (gamma prime) phase into account.

[0017]

According to the Ni-base superalloys of the present invention, the quantity ratio of Cr contributing to the resistance to corrosion in a multiple environment of sulfidation and oxidation, Al for generating the γ' phase and contributing to the high-temperature strength and resistance to oxidation, and Ti for contributing to the resistance to corrosion is within an appropriate range, and the reinforced elements mainly W whose additional quantity is decided by contribution to strength improvement and influence on corrosion resistance are added to the concerned quantity ratio, thus the resistance to corrosion at high temperatures, the

resistance to oxidation at high temperatures and high-temperature strength can be made excellent.

Further, the Ni-base superalloys can obtain sufficiently high strength for practical use in the columnar grain material state, so that there is no need to set single crystallization as a precondition.

Particularly, the second Ni-base superalloy is suitable for columnar crystalline blades or single crystalline blades by directional solidification casting and can exhibit the properties of corrosion resistance, oxidation resistance, and strength on a high level, and the third Ni-base superalloy is suited for polycrystalline blades by conventional casting or columnar crystalline blades by directional solidification casting, and can suppress the material cost while maintaining the properties of corrosion resistance, oxidation resistance, and strength.

Therefore, application of the present invention to turbine blades of an industrial gas turbine dealing with low-quality fuel is effective in improvement of the thermal efficiency and reliability of the gas turbine.

[0018]

Further, the gas turbine component of the present invention has better tolerance than the exclusive single crystal material for the reduction in strength due to casting defects such as low-angle grain boundaries or high-angle grain boundaries, and the allowable restriction range is wide, so that a high yield can be ensured at the casting process of gas turbine component in complicated shapes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

Fig. 1 is an illustration showing the results of the hot corrosion test for the Ni-base superalloys of the present invention and existing Ni-base superalloys.

Fig. 2 is an illustration showing the results of the high-temperature oxidation test for the Ni-base superalloys

of the present invention and existing Ni-base superalloys.

Fig. 3 is an illustration showing the results of the creep test for the Ni-base superalloys of the present invention and existing Ni-base superalloys.

BEST MODE FOR CARRYING OUT THE INVENTION

[0020]

Although Co expands the solution heat treatment temperature range, when the content thereof is less than 9 wt% (for the third alloy, 10 wt%), the effect cannot be obtained, and when it is more than 11 wt% (for the second alloy, 10 wt%), the deposition of the γ′ phase is reduced and the high-temperature strength is lowered.

[0021]

Although Cr particularly improves the resistance to corrosion in a multiple environment of sulfidation and oxidation, when the content thereof is less than 9 wt% (for the third alloy, 10 wt%), the effect cannot be obtained and when it is more than 12 wt% (for the second alloy, 10 wt%), a TCP (Topologically Close Packed) phase is generated and the high-temperature strength is lowered.

[0022]

Although Mo improves the high-temperature strength by solid solution reinforcement and deposition hardening, when the content thereof is more than 1 wt%, the resistance to corrosion is lowered.

Further, the second alloy, when the content of Mo is less than 0.5 wt%, cannot obtain the aforementioned effect.

[0023]

Although W improves the high-temperature strength by solid solution reinforcement and deposition hardening, when the content thereof is less than 6 wt% (for the third alloy, 8 wt%), the effect cannot be obtained, and when it is more than 9 wt% (for the second alloy, 8 wt%), the TCP phase is generated and the high-temperature strength is lowered.

Further, although W is generally considered to lower the

resistance to corrosion, knowledge that in the composition area of the present invention, there is few effect by W on the resistance to corrosion is obtained.

[0024]

Although Al generates the γ′ phase and improves the high-temperature strength and resistance to oxidation, when the content thereof is less than 4 wt%, the effect cannot be obtained, and when it is more than 5 wt%, the eutectic γ′ phase is increased in amount, and the solution heat treatment becomes difficult to be performed, and the resistance to corrosion is lowered.

[0025]

Although Ti improves the resistance to corrosion, when the content thereof is less than 4 wt%, the effect cannot be obtained, and when it is more than 5 wt%, the resistance to oxidation is lowered, and the heat treatment property is lowered.

[0026]

Although Nb is fused in the γ′ phase and improves the high-temperature strength, when the content thereof is more than 1 wt%, it is deposited in the grain boundaries, and lowers the high-temperature strength.

[0027]

Although Ta improves the high-temperature strength by solid solution reinforcement and deposition hardening, when the content thereof is more than 3 wt%, the eutectic γ′ phase is increased in amount, and the solution heat treatment becomes difficult to be performed.

Further, the second alloy, when the content of Ta is less than 2 wt%, cannot obtain the aforementioned effect.

[0028]

Although Hf reinforces the grain boundaries and improves the high-temperature strength and ductility and is effective to prevent intergranular cracking during DS casting, when the content thereof is less than 0.5 wt%, the effect cannot be obtained, and when it is more than 2.5 wt%, it segregates in

the grain boundaries, and lowers the high-temperature strength.

[0029]

Although Re improves the high-temperature strength by solid solution reinforcement and particularly improves the resistance to corrosion at 900°C or higher, when the content thereof is more than 3 wt%, the ductility is deteriorated by deposition of the TCP phase, and the specific gravity is increased, and the cost is increased.

Further, the second alloy cannot obtain the aforementioned effect when the content of Re is less than 1 wt%.

[0030]

Although C forms carbides and reinforces the grain boundaries, when the content thereof is less than 0.05 wt%, the effect cannot be obtained, and when it is more than 0.15 wt% (for the second alloy, 0.1 wt%), an excessive carbide is generated, and the high-temperature strength is lowered.

[0031]

Although B forms boronides and reinforces the grain boundaries, when the content thereof is less than 0.005 wt%, the effect cannot be obtained, and when it is more than 0.015 wt% (for the second alloy, 0.01 wt%), the ductility and toughness are lowered, and the high-temperature strength is lowered.

[0032]

Although Zr reinforces the grain boundaries, when the content thereof is more than 0.05 wt% (for the second alloy, 0.02 wt%), the ductility and toughness are lowered, and the high-temperature strength is lowered.

Further, the third alloy cannot obtain the aforementioned effect when the content of Zr is less than 0.01 wt%.

EMBODIMENTS

[0033]

Ni-base superalloys (alloys 1 to 3 of the present invention and comparison alloys 1 to 3) having the component composition

shown in Table 1 (the component compositions of the existing alloy 1 (Rene80H) and existing alloy 2 (Mar-M247) are also shown) are prepared, and these Ni-base superalloys are solidified under the condition of withdrawing speed 200 mm/h using a directional solidification casting furnace, and columnar crystalline castings are manufactured.

Next, the heat treatment indicated below is performed, thus the respective Ni-base superalloys are obtained.

Heat treatment conditions

Solution treatment: At 1200 to 1260°C, holding for 2 hours, then air cooling

Aging: First stage, at 1080°C, holding for 4 hors, then air cooling

Second stage, at 870°C, holding for 20 hours, then air cooling

[0034]

[Table 1]

	Ni	Co	Cr	Mo	W	Al	Ti	Nb	Ta	Hf	Re	C	B	Zr
Alloy 1 of present invention	Remainder	10	10	0.8	7	4	4	0	2.5	0.5	2	0.1	0.01	0.01
Alloy 2 of present invention	Remainder	11	11	0	8.5	4	4.5	0	0	1	0	0.11	0.01	0.05
Alloy 3 of present invention	Remainder	10	12	0.5	6	4	4.5	0.5	0	1	0	0.1	0.01	0.01
Comparison alloy 1	Remainder	12	8	0	5	6	2	0	4	1	2	0.07	0.015	0
Comparison alloy 2	Remainder	9	14	2	4	3	5	0	2	0.7	0	0.16	0.015	0.06
Comparison alloy 3	Remainder	9	10	3	4	3.5	5	0	2	0.7	0	0.16	0.015	0.06
Existing alloy 1	Remainder	9.2	13.9	4.1	4.1	3.1	4.8	0	0	0.7	0	0.16	0.015	0.06
Existing alloy 1	Remainder	10	8.3	0.7	10	5.5	1	0	3	1.5	0	0.15	0.015	0.05

(Unit: Weight %)

[0035]

For the test specimens of the alloys 1 to 3 of the present invention obtained and the existing alloys 1 and 2, the hot corrosion test is executed under the following conditions and the maximum corrosion depth of each test specimen obtained is shown in Fig. 1.

Test specimen shape: Diameter of 10 mm, length of 100 mm

Test conditions: In combustion gas with corrosive ingredients (sulfuric oil, artificial seawater) added into kerosene fuel, at a combustion gas temperature of 1050°C, air cooling after exposure for 100 hours, repeated 5 times (500 hours in total)

[0036]

Further, for the test specimens of the alloys 1 to 3 of the present invention obtained and the existing alloys 1 and 2, the oxidation test is executed under the following conditions and the mass change of each test specimen obtained is shown in Fig. 2.

Test specimen shape: Diameter of 10 mm, length of 25 mm

Test conditions: In the atmosphere, at 950°C, air cooling after exposure for 500 hours

[0037]

Furthermore, for the test specimens of the alloys 1 to 3 of the present invention obtained and the existing alloys 1 and 2, the creep test is executed under the following conditions and the rupture life of each test specimen obtained is shown in Fig. 3.

Test specimen shape: Diameter of 4 mm, gauge length of 24 mm

Test conditions: In the atmosphere, at 900°C, at 392 MPa

[0038]

On the basis of the existing alloy 1, the maximum corrosion depth ratio in the hot corrosion test, the mass change ratio in the oxidation test, and the rupture life ratio in the creep test for the alloys 1 to 3 of the present invention, the

comparison alloys 1 to 3, and the existing alloy 2 are checked and the results are shown in Table 2.

[0039]

[Table 2]

	Maximum corrosion depth ratio in hot corrosion test	Mass change ratio in oxidation test	Rupture life ratio in creep test
Alloy 1 of present invention	0.73	0.28	3.19
Alloy 2 of present invention	1.20	0.44	1.32
Alloy 3 of present invention	0.67	0.57	0.81
Comparison alloy 1	4.73	0.08	2.82
Comparison alloy 2	0.85	0.83	0.30
Comparison alloy 3	1.69	0.60	0.95
Existing alloy 1	1.00	1.00	1.00
Existing alloy 2	2.20	0.09	3.12

[0040]

As shown in Figs. 1 to 3 and Table 2, the alloy 1 of the present invention is excellent in the resistance to corrosion, resistance to oxidation, and strength and is particularly suited to use as a directional solidification material when higher strength is needed.

The alloy 2 of the present invention is suited to use under the condition that the resistance to oxidation and strength are needed, and the resistance to corrosion is within the tolerance to use the heavy oil fuel.

Further, the alloy 3 of the present invention is suited to use under the condition that the resistance to corrosion is needed.

[0041]

Although the existing alloy 1 is widely used as a turbine blade material of a gas turbine and is excellent in the resistance to corrosion, as compared with the composition range of the alloys 1 to 3 of the present invention, it contains much Cr and little Al, so that the resistance to oxidation is low, thus the existing alloy 1 cannot deal with high-temperature demands of combustion gas aiming at improvement of thermal efficiency.

Further, although the existing alloy 2 is excellent in the resistance to oxidation and strength, as compared with the composition range of the alloys 1 to 3 of the present invention, it contains little Cr and Ti and much Al, so that the resistance to corrosion is low, thus the existing alloy 2 cannot deal with heavy oil fuel.

[0042]

The comparison alloy 1 (almost corresponding to the composition range described in Japanese Patent Laid-Open Publication No. 5-59473 and Japanese Patent Laid-Open Publication No. 9-170402), as compared with the composition range of the alloys 1 to 3 of the present invention, contains little Ti, so that the resistance to corrosion is insufficient.

The comparison alloy 2 (almost corresponding to the composition range described in Japanese Patent Laid-Open Publication No. 9-170402), as compared with the composition range of the alloys 1 to 3 of the present invention, contains much Cr and little Al and W, so that the strength is insufficient.

Further, the comparison alloy 3 (almost corresponding to the composition range described in Japanese Patent Laid-Open Publication No. 5-59473), as compared with the composition range of the alloys 1 to 3 of the present invention, contains much Mo, so that the resistance to corrosion is insufficient.

[0043]

Although the invention has been described in its preferred embodiment with a certain degree of particularity, obviously many changes and variations are possible therein. It is therefore to be understood that the present invention may be practiced otherwise than as specifically described herein without departing from the scope and spirit thereof.